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PHASE COMPOSITION OF CERAMIC BRICK FROM THE KREMLIN IN ASTRAKHAN

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Investigations have shown that the strength of the ceramic brick in the Astrakhan kremlin is mainly due to mullite. The crystallization of mullite in the experimental specimen shows that the firing temperature of the brick was less than 1000 – 1050°C.

Key words: x-ray phase analysis, IR spectrum, electron microscope, phase composition, ceramic brick, Astrakhan kremlin, firing temperature, mullite.

The structure of serviceable ceramic articles is formed during the firing process [1]. In the chemical technology of ceramic materials the question of phase transformations is given special attention, since the phase composition determines, first and foremost, the performance properties of ceramic materials [2].

The complexities and difficulties of the present stage of the historical evolution of our domestic brick industry are associated not only with new problems but also with a discontinuity between the times — a sharp gap between the science of the last ten years and the study and analysis of historical experience [2, 3]. Understanding how the past, present and future are interrelated makes it possible to bridge the gap between our understanding of how ceramic materials were produced in the past and the best way to proceed in our global post-industrial information society in the 21st century [2].

The modern methods of chemical analysis make it possible to determine the phase compositions of ceramic materials of any age [2].

The kremlin in Astrakhan is the city's focal point and crown jewel, its main point of interest, a living chronicle and a unique historical and architectural museum and preserve (Fig. 1*a*). The history of the Krai is imprinted in its marvelous structures. It is an "eminent witness of the city's history."

Astrakhan became the second city in Russia where a stone kremlin was built. The Astrakhan kremlin provided graphic confirmation of the military and political might of the Russian government.

The stone kremlin built in Astrakhan at the location of wooden structure and excavations is a remarkable monument

a

b

Fig. 1. The kremlin in Astrakhan: *a*) kremlin at the city limits; *b*) location where the brick used for the investigations was collected.

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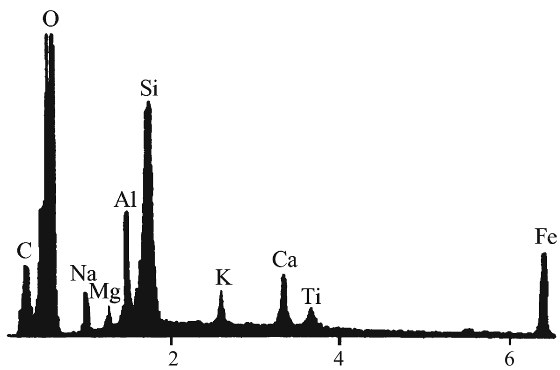

Fig. 2. X-ray spectral microanalysis of a ceramic sample from the wall of the Astrakhan kremlin.

to the architecture of Russian fortresses in the second half of the 16th century, the strongest military-engineering fortification at that time. All advances in military science of that time were used to make this fortress an impregnable stronghold. In terms of scales this was truly an all-Russian construction project: the kremlin took seven years to build (1582 – 1589).

Brick, imported from the ruins of the Golden Horde cities, served as the main material for the kremlin's fortress walls and towers.

The more than 400-yr old ceramic material has been studied using the following:

– x-ray phase analysis using a DRON-6 diffractometer with CoK_α radiation;

– an FEI Quanta Inspect S electron microscope with an EDAX Genesis attachment and an ultrathin window as well as an ÉMB-100BR electron microscope;

– method of replicas in transmission;

– determination of the chemical elemental composition.

The IR absorption spectra of the ceramic specimens were obtained with a Specord-75JR spectrophotometer. The samples were prepared in the form of a suspension of powder with mineral oil.

The location where the brick was collected from the wall of the Astrakhan kremlin is shown in Fig. 1*b*.

Elemental analysis showed that the main chemical elements present in the samples are Si, Al, Fe, C, Ca and Na (Fig. 2).

The chemical compositions (oxide and elemental) of the ceramic samples from the wall of the Astrakhan kremlin are presented in Table 1. As one can see from the data in Table 1, the samples have an elevated content of iron and alkali oxides, which in turn promote the formation of a liquid phase at temperatures below 950°C [1]. The liquid phase lowers the onset of crystallization of mullite.

In clays iron oxide is present mainly in the form of impurities and imparts, after firing, predominately a reddish color; but, for Fe_2O_3 content above 5% the color ranges from light to dark Bordeaux (provided that the CaO content in the clays does not exceed 7 – 8%) [4].

TABLE 1. Chemical Compositions of Samples from a Wall of the Astrakhan Kremlin

Composition, wt.%

Oxide

SiO_2	$Al_2O_3 + TiO_2$	Fe_2O_3	CaO	MgO	R_2O
55.1	18.1	8.84	7.01	2.02	5.52

Elemental

O	Si	Al	Fe	Ca	Na	K	Mg	C	Ti
42.88	21.14	9.48	7.08	5.01	3.61	2.44	1.24	6.28	0.84

The high carbon content (C = 6.28%) in the ceramic brick shows that burnable additives were introduced into the batch [2]. They are added in amounts to 3 vol.%, i.e., 60 – 80% of the total fuel consumption for firing an article [2, 4]. The iron oxides lower the melting temperature of the clay appreciably only if the firing is conducted in a reducing medium, which is created by introducing fuel into the composition of the brick.

It was shown in [2, 5] that elevated iron oxide promotes crystallization of mullite at the early stages of firing (1000 – 1050°C).

Mullite imparts the basic properties to ceramic materials. The frost, acid and heat resistance as well as the strength of the articles depend on the structure and amount of mullite formed during the firing process [2, 5].

An x-ray diffraction pattern of the kremlin brick from Astrakhan is displayed in Fig. 3*a*.

The following characteristic strong lines are observed in the diffraction pattern of the powder: quartz — $d/n = 0.184$, 0.205, 0.222, 0.230, 0.342 and 0.443 nm; hematite — $d/n = 0.169$, 0.184, 0.220, 0.244, 0.251, 0.269 and 0.365 nm; mullite — $d/n = 0.184$, 0.200, 0.211, 0.220, 0.242, 0.254, 0.269, 0.339 and 0.376 nm; anorthite — $d/n = 0.177$, 0.215, 0.294, 0.321, 0.376 and 0.429 nm; feldspar — $d/n = 0.237$, 0.256, 0.276, 0.290, 0.347 and 0.361 nm; and, cristobalite — $d/n = 0.173$, 0.192, 0.246, 0.283, 0.313 and 0.403 nm.

As one can see from Fig. 3*a*, the minerals anorthite, cristobalite, hematite and mullite form in the fired brick from the Astrakhan kremlin. The formation of these minerals in the samples studied is also confirmed by the increase in the IR absorption bands (Fig. 4): $\nu = 1100$ and $1010\ cm^{-1}$ for cristobalite; $\nu = 1182$, 1130 and $1090\ cm^{-1}$ for mullite; and, $\nu = 870$ and $472\ cm^{-1}$ for anorthite and hematite, respectively.

To obtain more complete information on structure formation in the brick from the Astrakhan kremlin the microstructure of the brick was studied by the transmission replica method using an ÉMB-100BR electron microscope (Fig. 4).

Regions with a glass phase of significant size are presented in Fig. 4*a* and *b*. Small, slightly fused, quartz crystals with a rhombohedral habit, small and medium-size feldspar

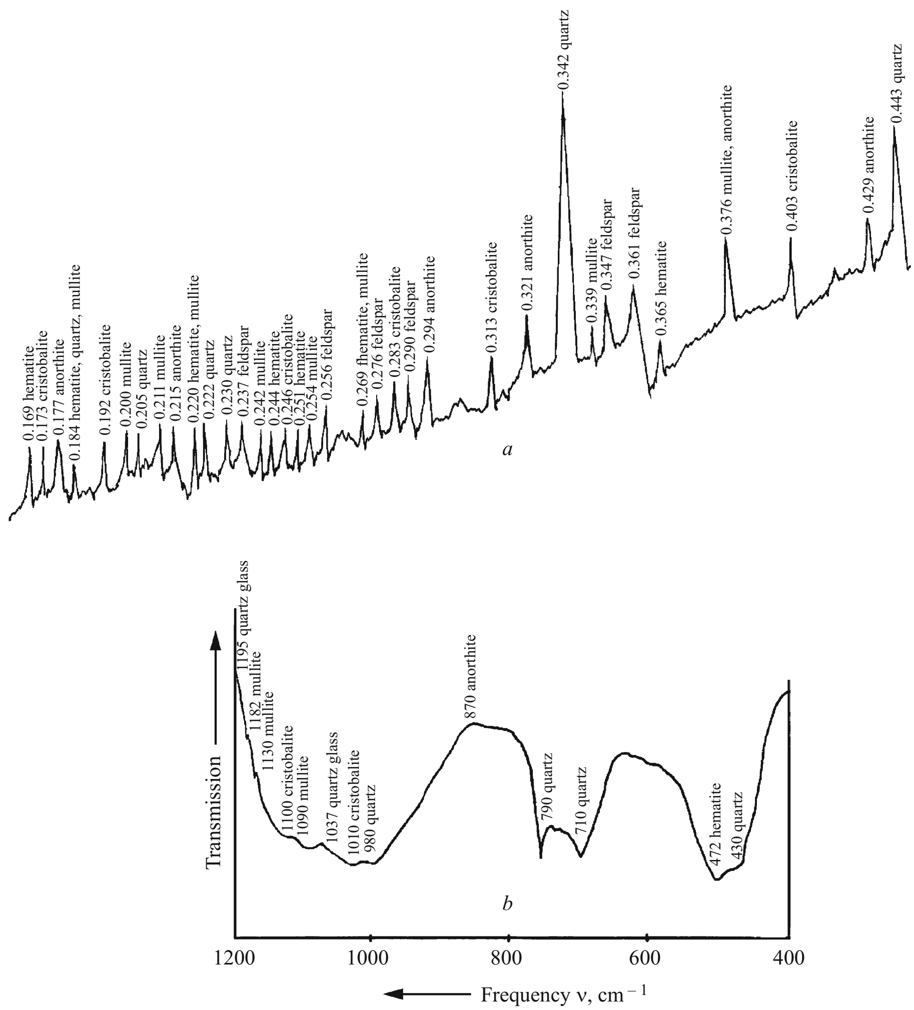

Fig. 3. X-ray phase and IR-spectroscopic analysis of the brick from the Astrakhan kremlin.

crystals with octahedral habit, individual micropores and hematite and anorthite crystals with tabular habit are present.

Individual crystals with short-columnar habit and aggregates of mullite crystals with needle habits are present in Fig. 4*c* and *d*. In addition, individual, large, tetragonal crystals of α-cristobalite are present in Fig. 4*c* [1, 5].

As one can see from Fig. 4, the following phases are observed in the Astrakhan kremlin brick: quartz with a fusion rim, pseudo-morphisms of glass with short-prismatic and needle-shaped mullite; cristobalite forms plate-shaped crystals up to 5 μm in size, which are ordinarily present in the anorthite-free sections of the glass phase, which form overgrowths one or several stories high.

In concluding the description of the studies of mullite formation during firing of brick it is useful to present thermodynamic calculations performed by some authors to confirm the possibility of mullite formation at relatively low firing temperatures (1000 – 1050°C), since many authors [6, 7] assert that mullite formation is impossible at the indicated temperatures.

Unfortunately, the published experimental data on the thermodynamic constants for silicates and other compounds widely used in silicate technology are very limited because

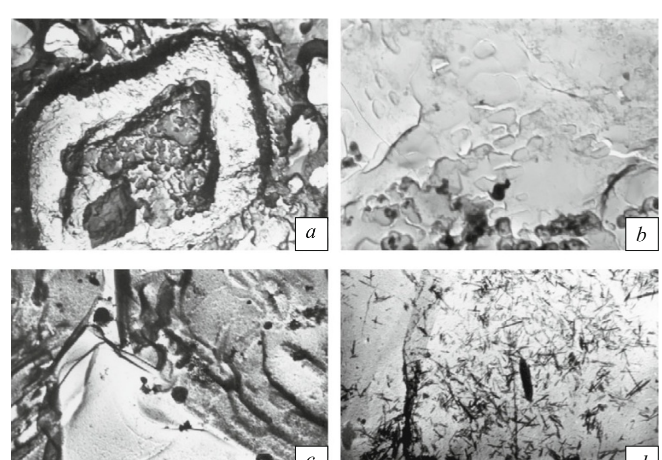

Fig. 4. Electron-microscopic photographs of thin sections of brick from the Astrakhan kremlin.

of special experimental difficulties arising in obtaining such data. This makes it necessary to use approximate methods to calculate the missing initial data. For this reason the authors of [8] thought it useful to present some approximate methods for calculating thermodynamic constants with an indication of their regions of applicability. In most cases these methods make it possible to obtain the thermodynamic constants with accuracy $\pm(3-5)\%$, which is completely acceptable for practical applications.

The equation expressing the temperature dependence of the heat capacity of the initial substances and products is $C_p = f(T)$ [8], where, usually, tabulated approximate equations of the type $C_p = a + bT + cT^2$ are used. For this reason, for $S^0_{298} = 60$ eu [cal/(mole · K)] (S^0_{298} is the entropy of the reaction at 298 K) and $T_{melt} = 1850°C$ (the melting temperature of mullite), the following equation was obtained in [9]:

$$C_p = 115.9 + 11.2 \times 10^{-3}T - 37 \times 10^5 T^2.$$

The quantities $\Delta H^0 = f(T)$ and $\Delta Z = f(T)$ for the formation of mullite from oxides were calculated using the experimental value $\Delta Z^0_{1823} = -5.95$ kcal/mol as follows [32]:

$$\Delta S^0_{1823} = \Delta S^0_{298} + \int_{298}^{848} (C_{p1}/T)\mathrm{d}T + \Delta S_{tr} + \int_{848}^{1823} (C_{p2}/T)\mathrm{d}T .$$

According to the Gibbs–Helmholtz equation $\Delta Z = \Delta H - T\Delta S$, the reaction enthalpy for the formation of mullite from oxides was determined from the equation [9]

$$\Delta H^0_{1823} = \Delta Z^0_{1823} + 1823\Delta S^0_{1823} = 6866 \text{ kcal/mol},$$

whence

$$\Delta H^0_{298} = \Delta H^0_{1823} - \int_{298}^{848} C_{p1}\mathrm{d}T - \Delta H^0_{tr} \int_{848}^{1823} C_{p2}\mathrm{d}T,$$

where C_{p1} is the heat capacity of β-quartz, C_{p2} the heat capacity of α-quartz, ΔS_{tr} the entropy change in the transformation and ΔH^0_{tr} the enthalpy change in the transformation.

These equations were used to calculate ΔH^0_T and ΔZ^0_T for the formation of mullite from oxides in the temperature interval 298 – 2000 K. In [9] these data were used to construct plots. The curve $\Delta H^0 = f(T)$ consists of two sections which are separated in the interval 298 – 2000 K by the point of the transformation β-quartz → α-quartz at 848 K.

According to the data in [9] the relation $\Delta Z^0 = f(T)$ is almost a straight line, especially at high temperatures. The intersection of this line with the zero ordinate ($\Delta Z^0 = 0$) occurs at the approximate temperature 944 K. The author of [9] is of the opinion that mullite is not formed below this temperature.

CONCLUSIONS

The investigations showed that the strength of the ceramic brick from the kremlin in Astrakhan is mainly due to mullite. The crystallization of mullite in the experimental sample attests that the firing temperature of the brick was at least 1000 – 1050°C.

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